Attrition-Resistant Iron-Based Catalyst for F-T SBCRS

Adeyinka A. Adeyiga

DOE-Massie Chair of Excellence
Department of Chemical Engineering, Hampton University, Hampton, VA 23668

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Presenter Information

Adeyinka A. Adeyiga
Department of Chemical Engineering
Suite 318, Olin Engineering Building, Hampton University
Hampton, VA 23668
Phone: (757) 727-5289
Fax: (757) 727-5189
Email: adeyinka.adeyiga@hamptonu.edu

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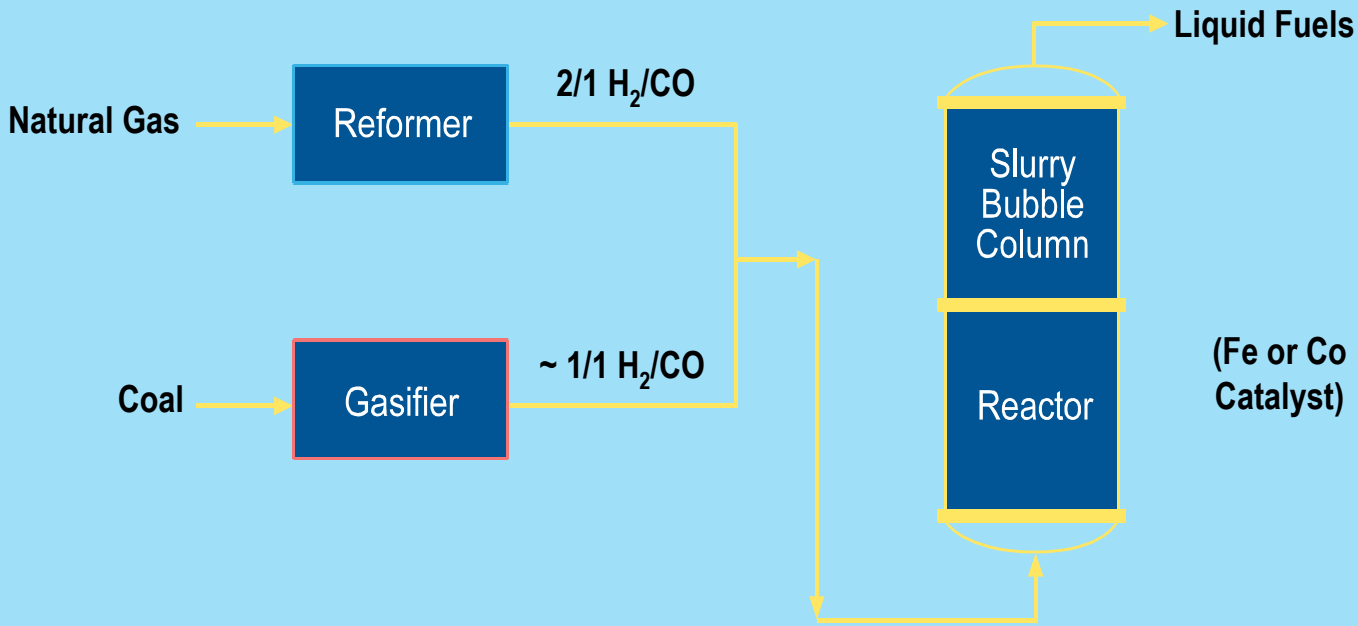
Background


Natural Gas
Reformer
2/1 H_2/CO
Coal
Gasifier
~ 1/1 H_2/CO
Slurry Bubble Column
Reactor
Liquid Fuels
(Fe or Co Catalyst)

Objective

To develop robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry bubble column reactor.

- Improve the performance and preparation procedure of the high activity, high attrition resistant, high alpha iron-based catalyst synthesized at Hampton University;
- Seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst preparation steps and,
- Investigate the performance in a slurry reactor.

Reactions

$$CO + 2\,H_2 \rightarrow -CH_2- + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$2\,CO + H_2 \rightarrow -CH_2- + CO_2$$

Advantages of Iron Catalysts

- Inexpensive
- Specific activity for FT synthesis is high
- Water-gas shift activity
- Convert low H_2/CO ratio syngas

Advantages of Slurry Bubble Column Reactor

- Ability to remove heat and control reaction temperature
- High rate of reaction/productivity

Problem

- Attrition of the iron catalysts in fixed bed reactors
- Attrition of the iron catalysts in downstream filters in slurry bubble column reactors
- Leading to activity decline because of loss of catalyst from the reactors

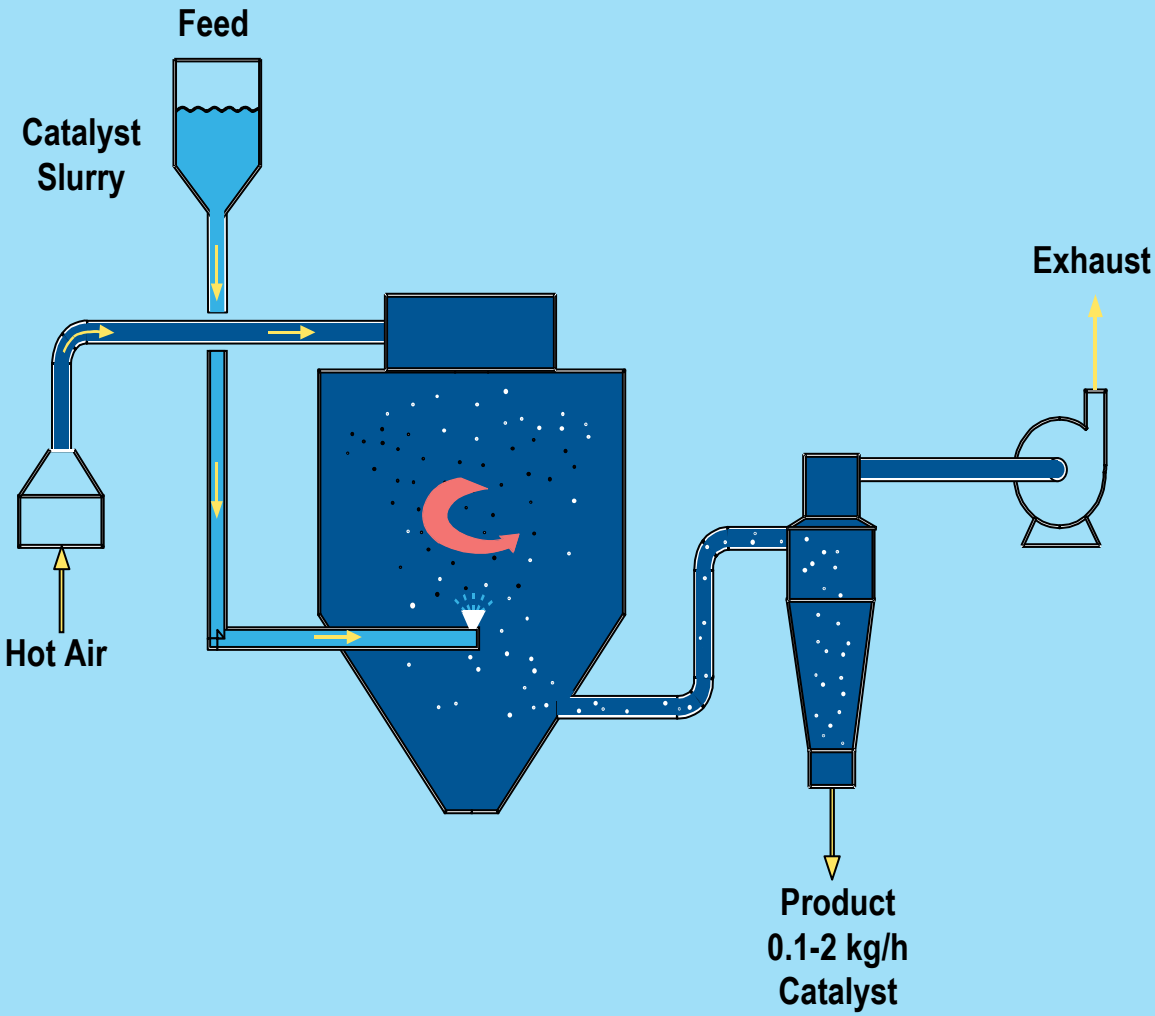
Remedy

To improve the physical strength of Fe FT catalysts, the spray-drying technique has been used for catalyst preparation without lowering catalyst activity

Catalyst Preparation

- Typical Fe FT catalysts is 100 Fe/5 Cu/4.2 K/*x* SiO_2
- Prepare a solution containing $Fe(NO_3)_3 \bullet 9H_2O$ of appropriate concentration
- Prepare a solution containing CU $(NO_3)_2 \bullet 2.5\ H_2O$ of appropriate concentration
- Take appropriate concentration of $Si(OC_2H_5)_4$
- Precipitation is carried using ammonium hydroxide (NH_4OH)
- Aqueous potassium in form of $KHCO_3$ is added to the slurry
- Slurry is spray dried at 250^oC in Niro spray drier
- The spray dried catalyst is then calcined at 300^oC for five hours in a muffle furnace
- The calcined catalysts were sieved between 38 and 90 μm

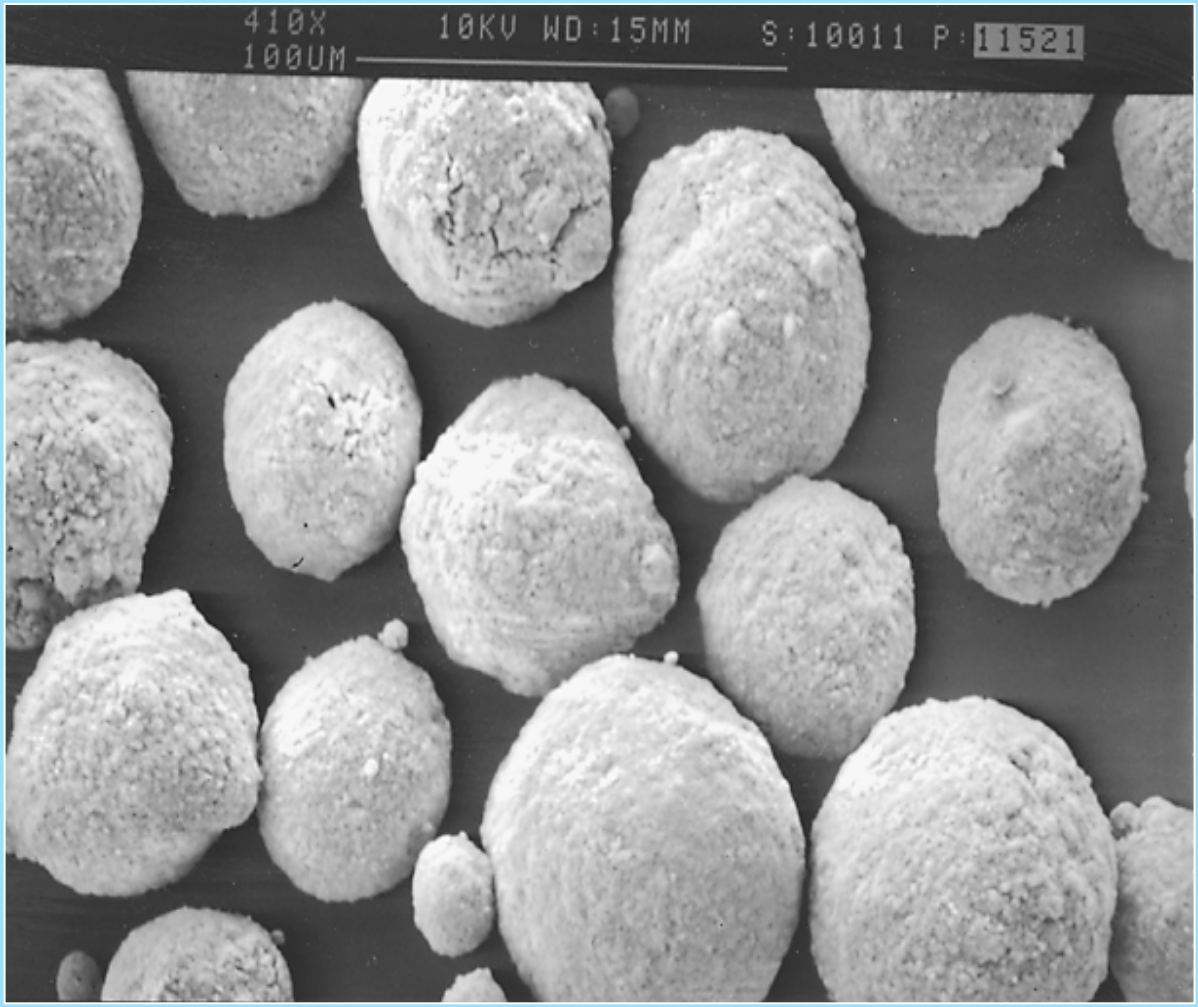
Niro Spray Drier



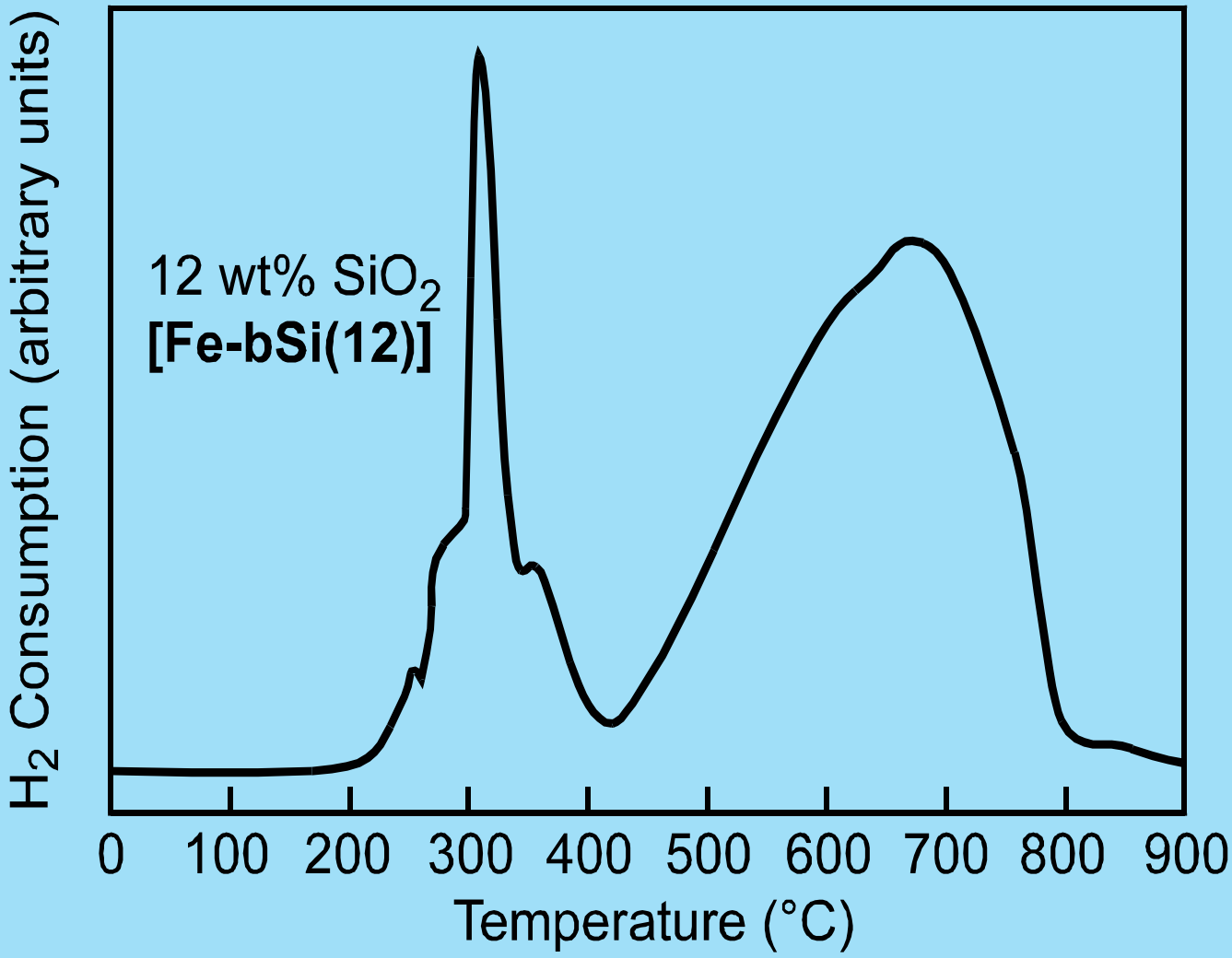
Catalyst Characterization Methods Employed

- BET
- Mercury porosimetry
- H_2-TPR
- SEM
- Metals analysis by AA
- Jet Cup

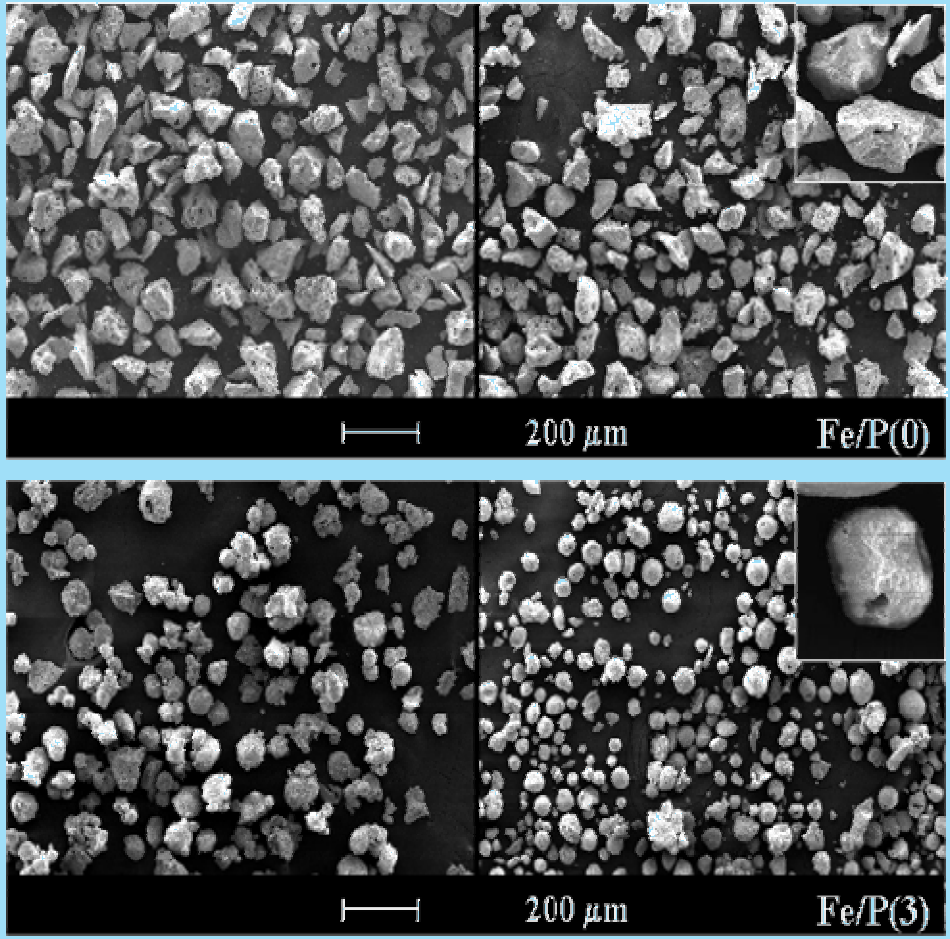
SEM Micrograph of Reduced Iron Catalyst



Hydrogen TPR of Iron Catalyst



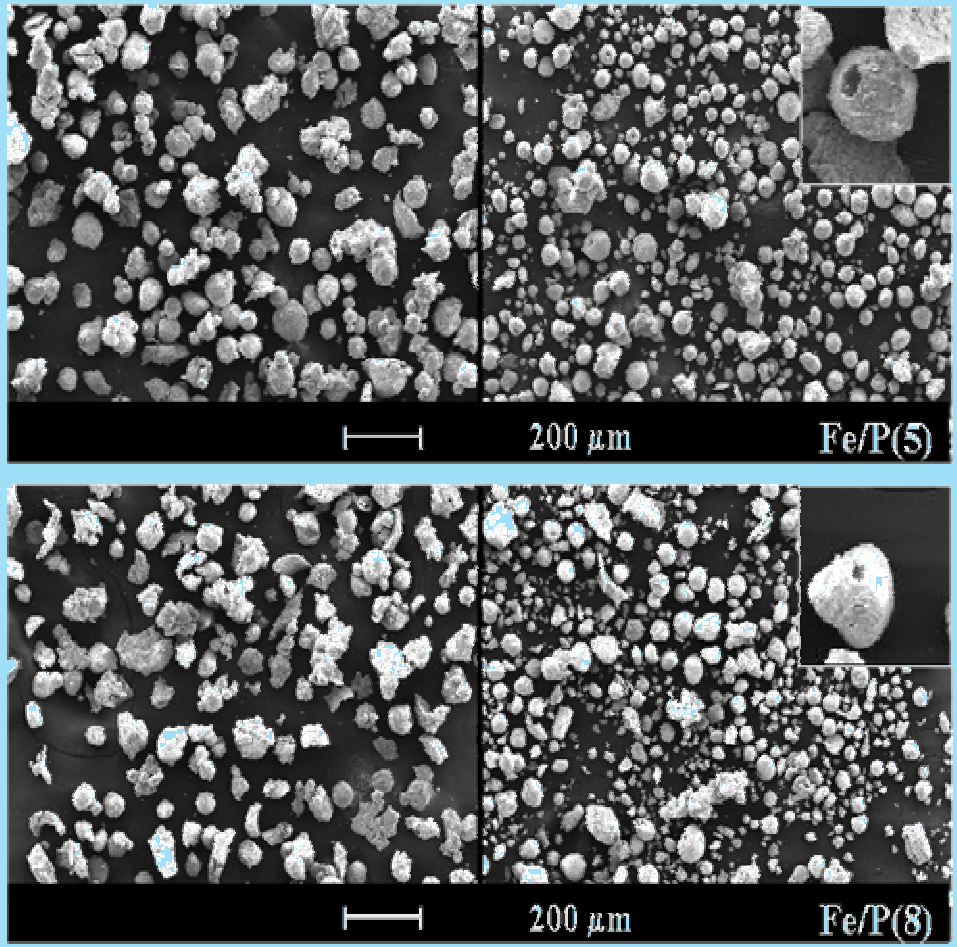
SEM Micrographs of Fe/P(0) and Fe/P(3) Before and After Attrition



Before Attrition

After Attrition

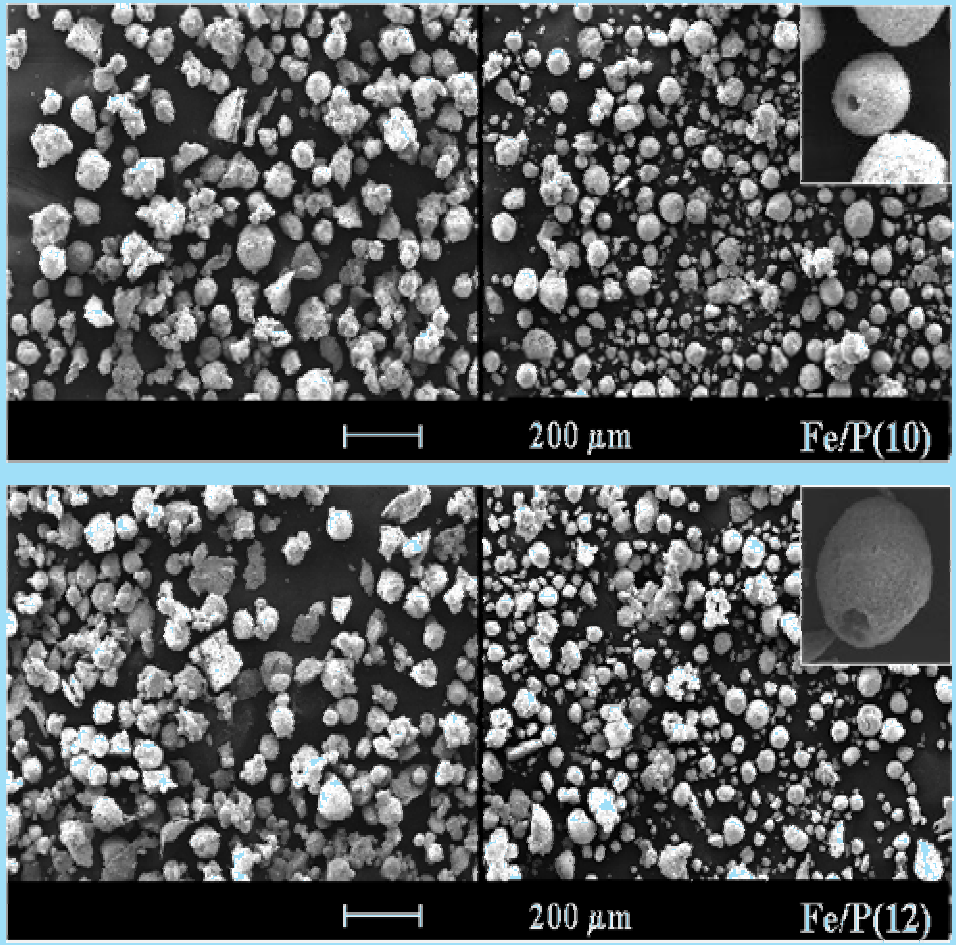
SEM Micrographs of Fe/P(5) and Fe/P(8) Before and After Attrition



Before Attrition

After Attrition

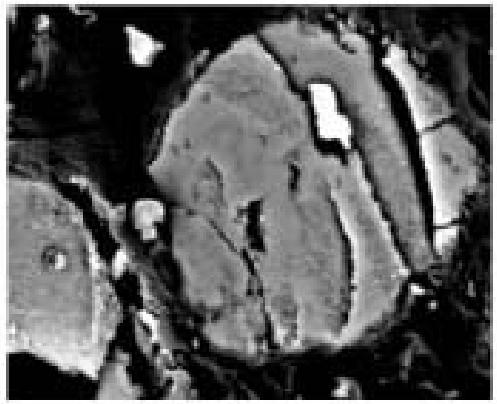
SEM Micrographs of Fe/P(10) and Fe/P(12) Before and After Attrition



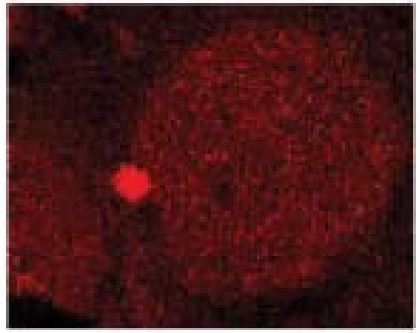
Before Attrition

After Attrition

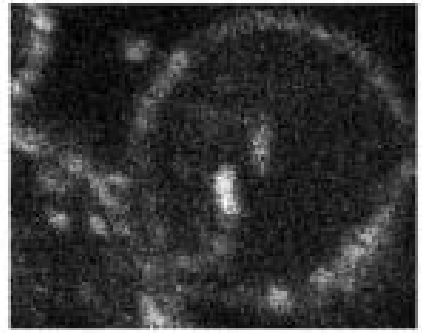
EDXS Results for the Cross Section of a Typical Fe/P(5) Particle



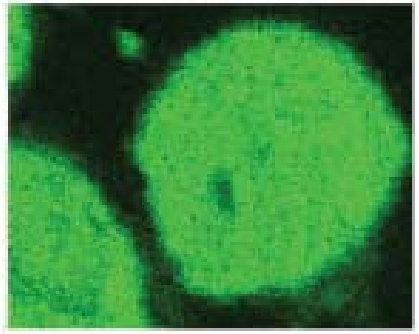
SEM image of Fe/P(5) cross section



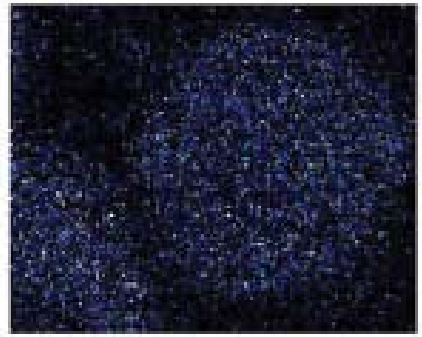
Si



K

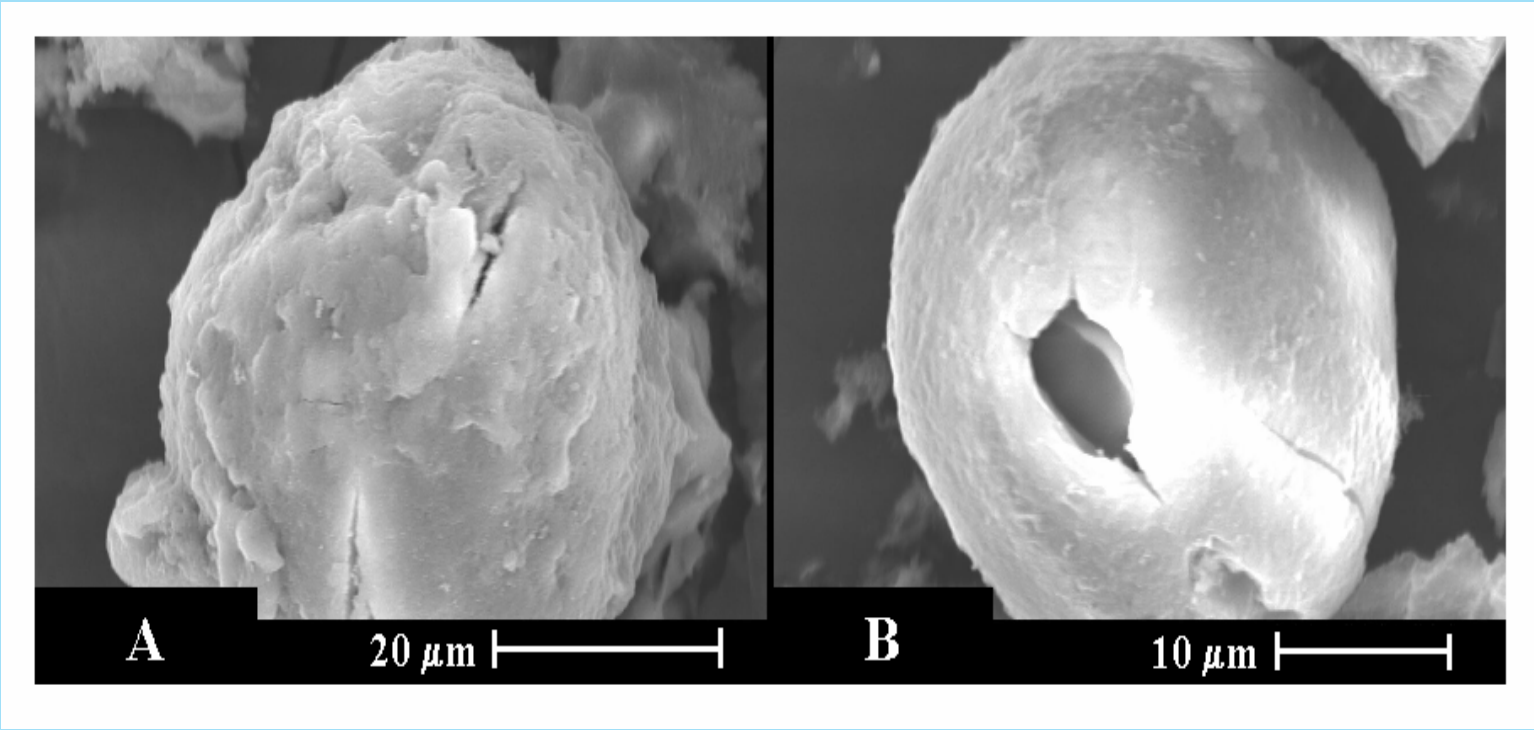


Fe



Cu

SEM Micrographs of Typical SiO_2 Structures After Acid Leaching [Fe/P(12)]



(A) Typical structure

(B) Particle with interior

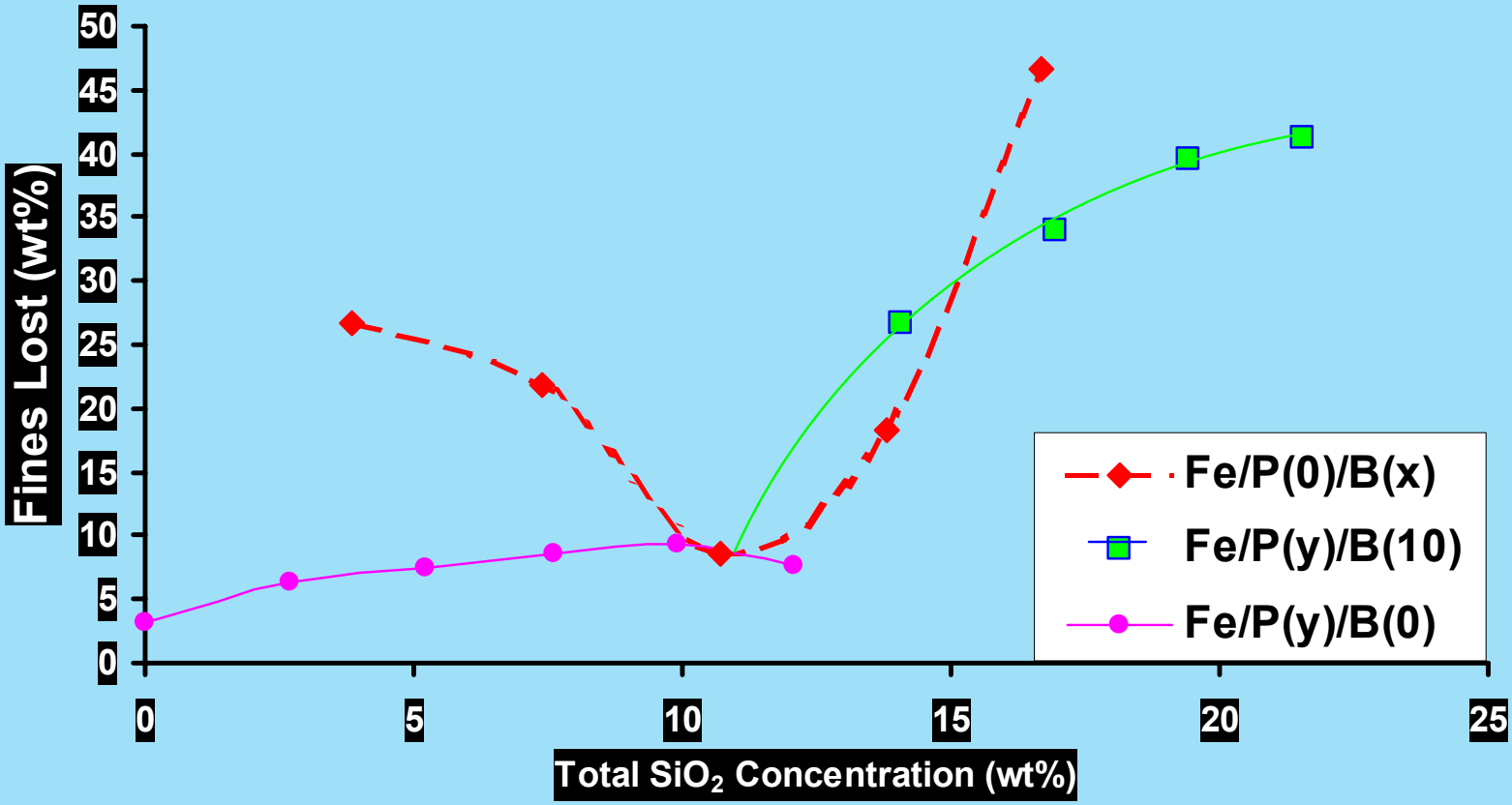
Jet Cup Attrition Test

- Attrition tests were conducted using a jet cup system
- In the jet cup test, 5g of each calcined catalyst sample was evaluated for attrition resistance under identical testing conditions using an air jet flow of 15 L/min with a relative humidity of 60 + 5% at room temperature and atmospheric pressure
- After 1 hr. time-on-stream, the air jet flow was stopped, and the weight of fines collected by the downstream filter was determined
- The “weight percentage of fines lost” was calculated and used as one of the attrition indices
- The particle size distribution before and after attrition testing was determined with a Leeds & Northup Microtrac laser particle size analyzer and used to calculate the “net change in volume moment”, the other attrition index used in our attrition studies. The volume moment is a measure of the average particle size.

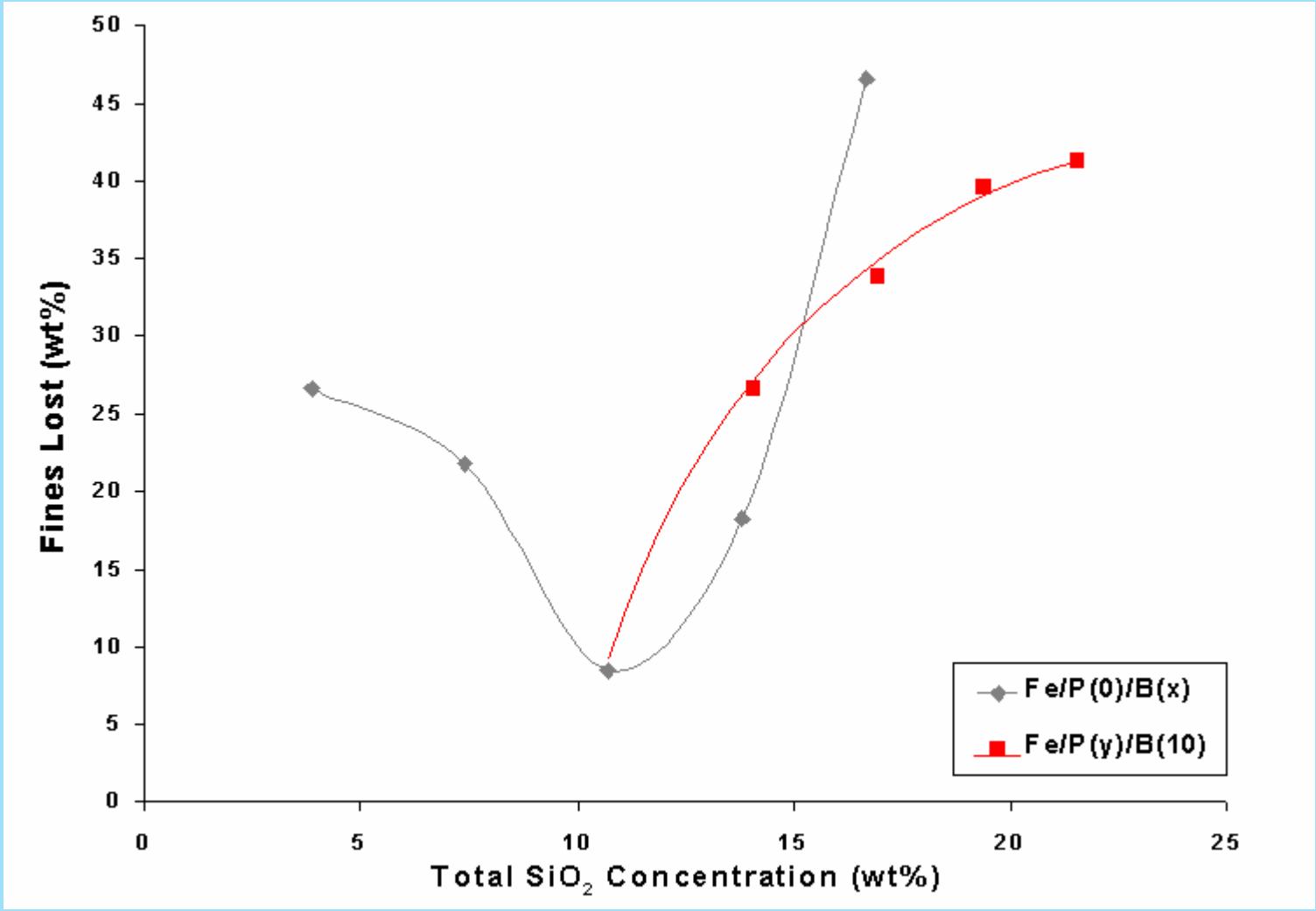
Jet cup attrition resistance test results

Catalysts	Attrition, wt %
Fresh (calcined)	4.8
CO pretreated	3.06
H_2/CO pretreated	3.85
H_2 pretreated	4.02

Attrition Results
(Jet Cup)



Attrition Test of Fe FT Catalysts

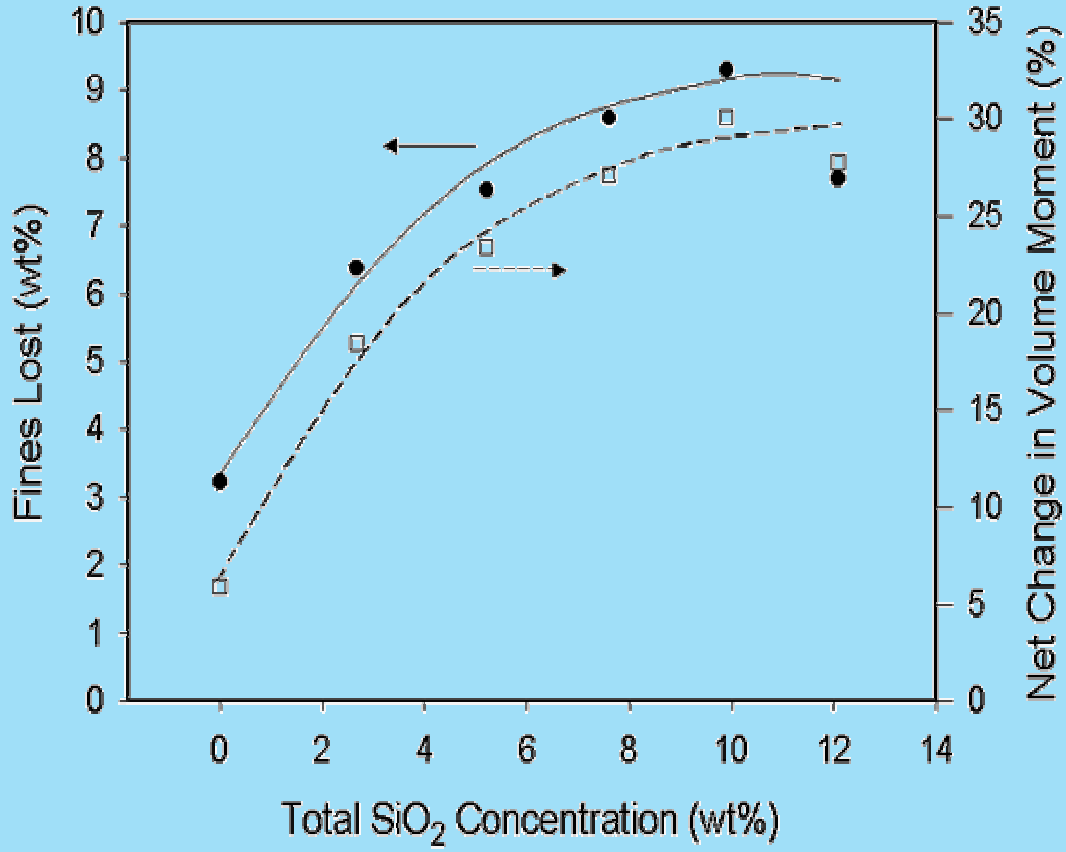


Jet Cup Attrition Results

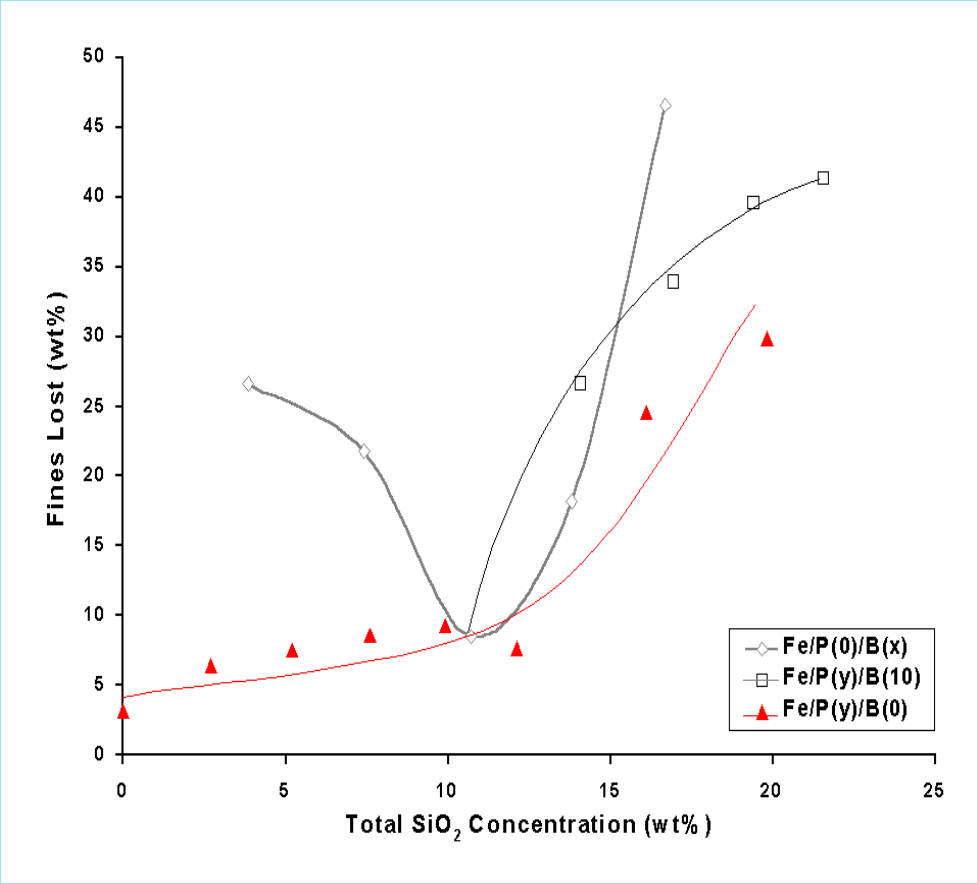
Catalyst	Total SiO_2 Concentration (wt%)	Fines Lost (wt%) (a,b)	Net Change in Volume Moment (5) (c,d,e)
Fe/P(0)	0.0	3.2	6.0
Fe/P(3)	2.7	6.4	18.4
Fe/P(5)	5.2	7.5	23.4
Fe/P(8)	7.6	8.6	27.1
Fe/P(10)	9.9	9.3	30.1
Fe/P(12)	12.1	7.7	27.8
Fe/P(16)	16.1	24.5	---
Fe/P(20)	19.8	29.9	---

(a) Wt% fines = weight of fines collected/weight of total catalyst recovered x 100%
(b) Error = $\pm$10% of the value measured.
(c) Net change in volume moment was determined with reference to the particle size distribution before attrition testing.
(d) Net change in volume moment (VM) = [(VM of sample after attrition test – VM of sample before test) / VM of sample before test] x 100%.
(e) Error = $\pm$5% of the value measured.

Jet Cup Attrition Results

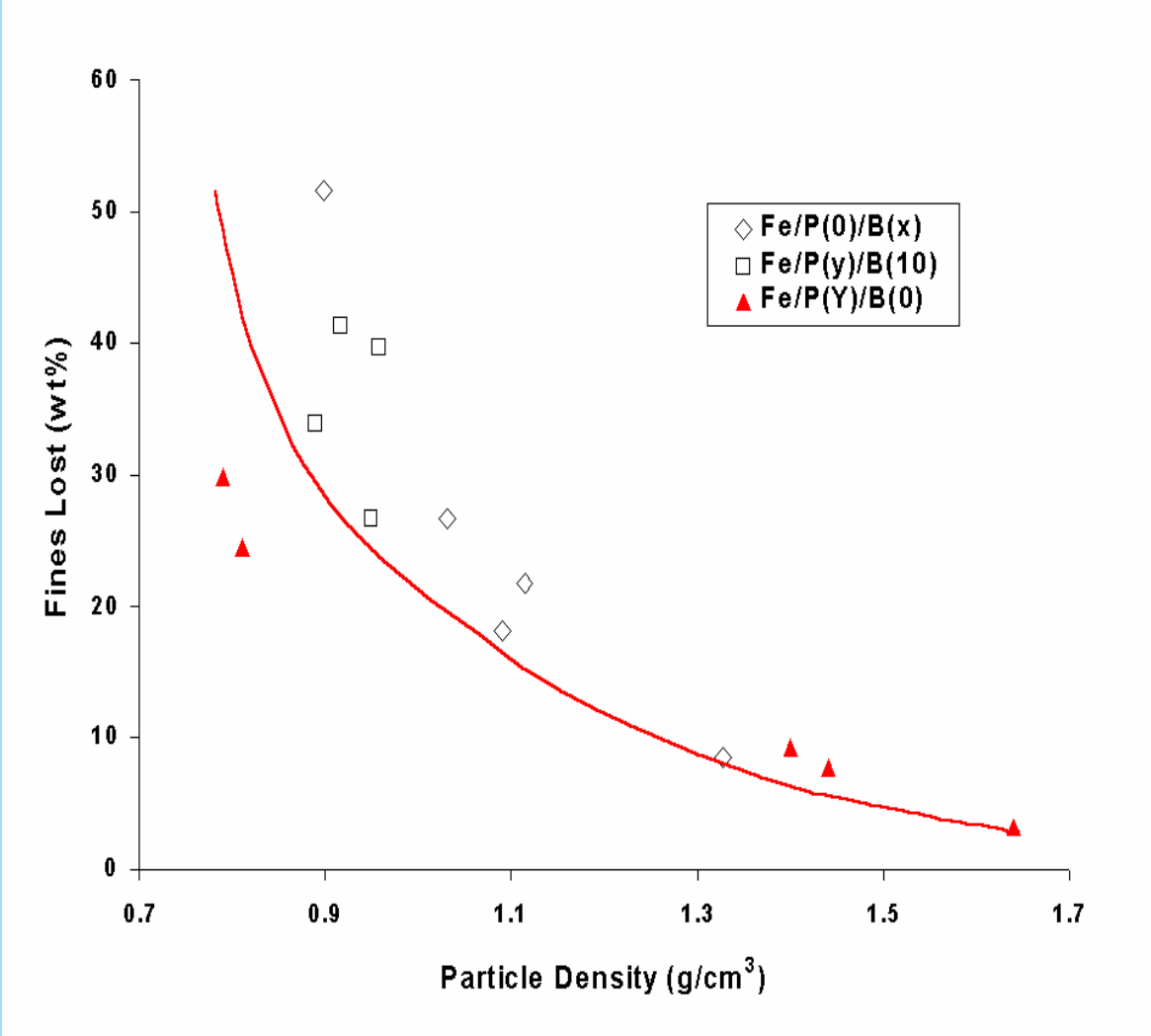


Weight Percentage of Fines Lost vs. Total Concentration of SiO_2 for Different Series of Spray-Dried Fe FT Catalysts



B refers to binder SiO_2; P refers to precipitated SiO_2; *x* and *y* refer to the amount of binder and precipitated SiO_2 added, respectively.

Weight Percentage of Fines Lost vs. Average Particle Density of Calcined Fe/P(*y*), Fe/B(*x*), and FE/P(*y*)/B(10) Catalysts



BET Surface Area and Pore Volume of the Iron Catalysts Studied

Table 2. BET Surface Area and Pore Volume of the Iron Catalysts Studied.

Catalyst	BET Surface Area (m^2/g) [a]		Pore Volume (cm^3/g) [b]	
	Fresh	Attritted	Fresh	Attritted
Fe/P(0)	24	23	0.08	0.08
Fe/P(3)	69	63	0.12	0.11
Fe/P(5)	83	115	0.12	0.16
Fe/P(8)	48	69	0.11	0.14
Fe/P(10)	41	44	0.11	0.11
Fe/P(12)	76	84	0.11	0.12

(a) Error = ±5% of the value measured.

(b) Error ≡ ±10% of the value measured.

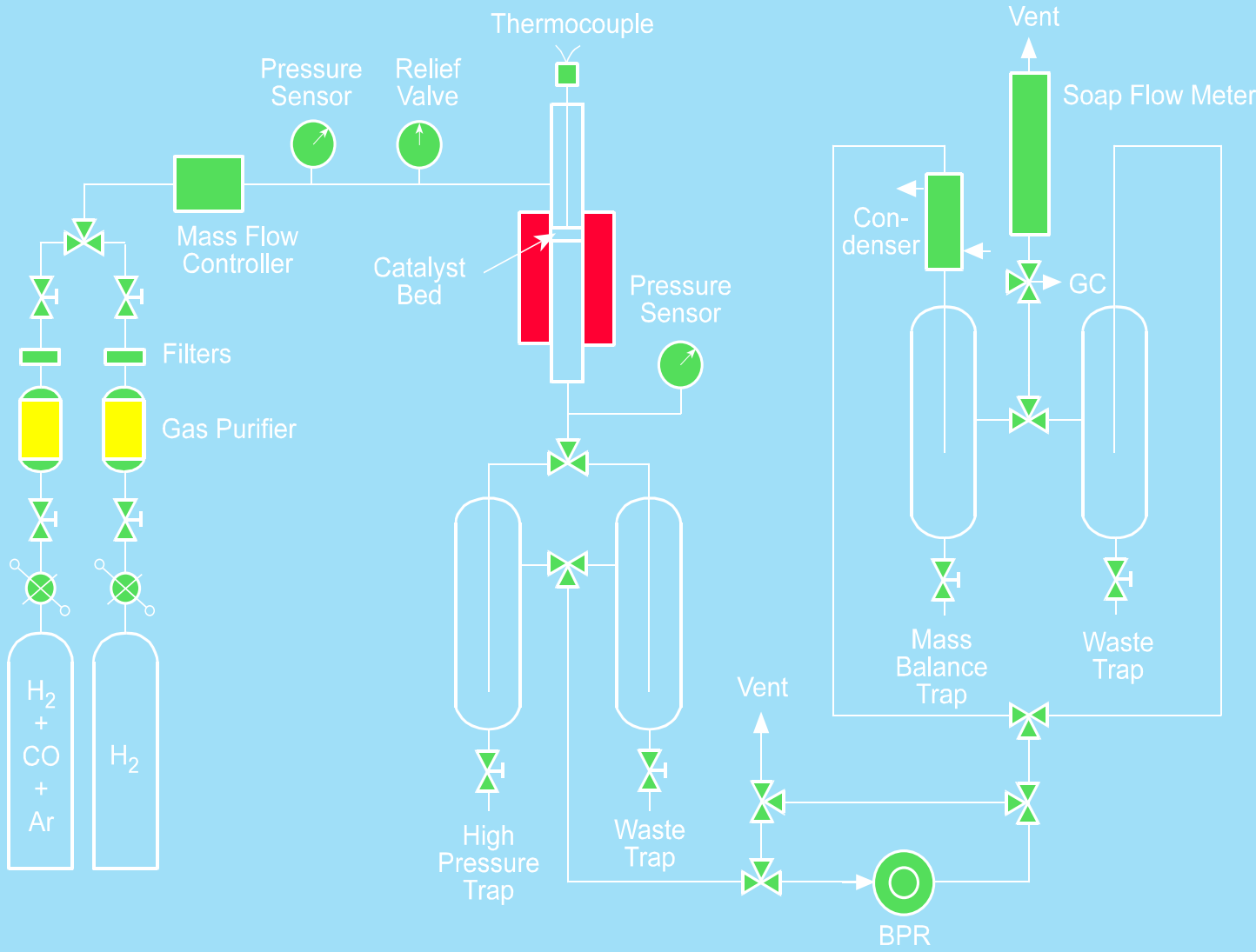
Macro Pore Volume and Particle Density of Selected Iron Catalysts

Catalyst	Macro Pore volume (cm^3/g) [a]	Particle Density (g/cm^3) [b]
Fe/P(0)	0.25	1.64
Fe/P(10)	0.26	1.40
Fe/P(12)	0.24	1.44
Fe/P(16)	--	0.81
Fe/P(20)	--	0.79

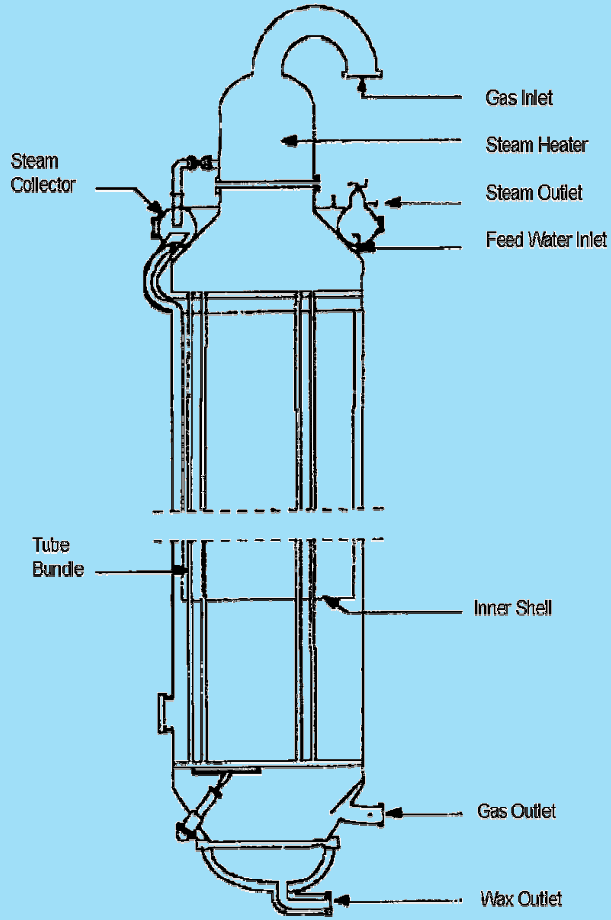
(a) Measured using mercury porosimetry, error ≡ ±10% of the valued measured.

(b) Determined using low-pressure mercury displacement, error = ±5% of the value measured.

FT Reaction Fixed-Bed Test Apparatus



Tubular Fixed Bed (ARGE) Reactor



Experimental Conditions

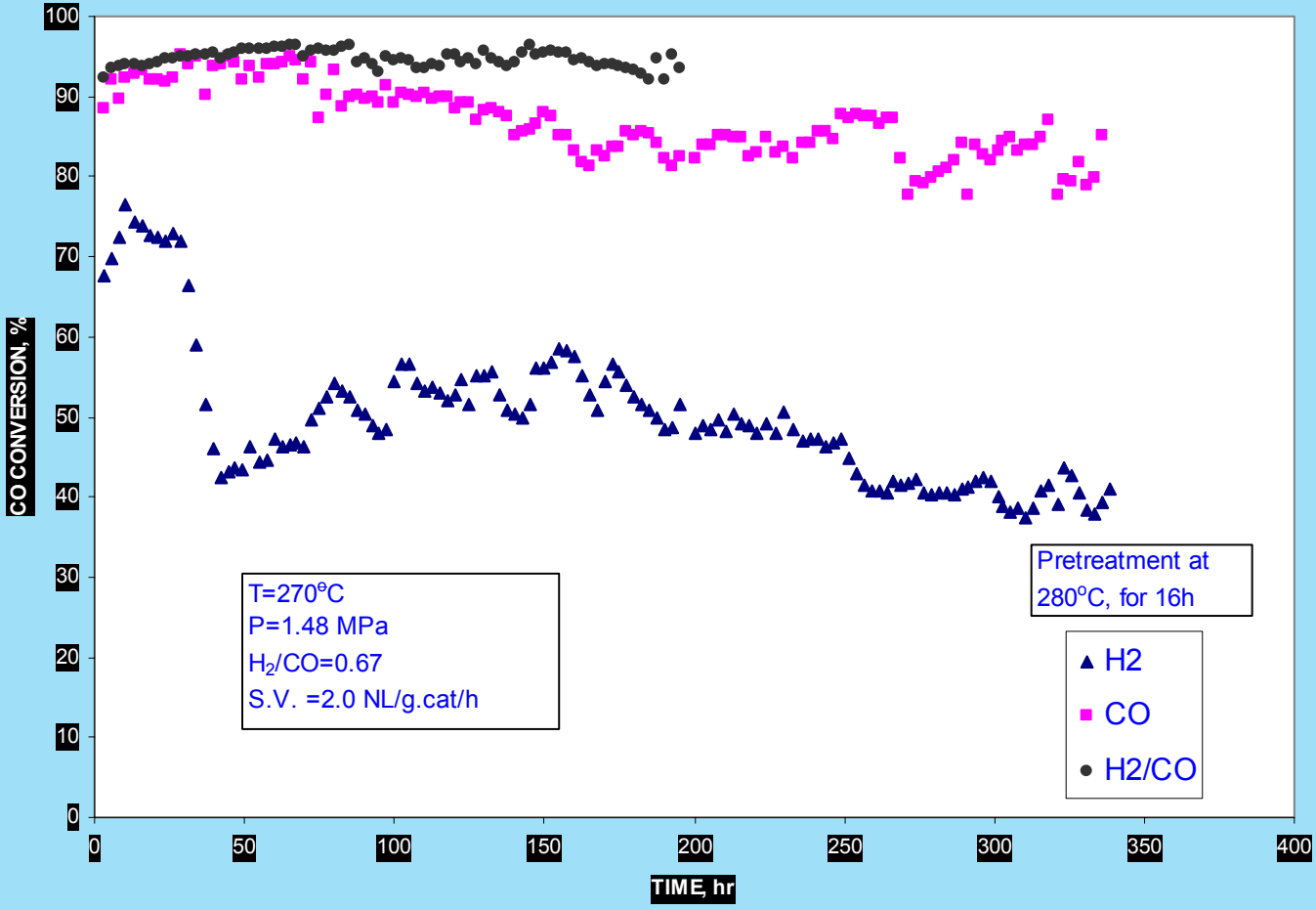
- Activation

  0.1 MPa, 280 °C, CO, H_2, CO+H_2, 16 h

- Reaction

H_2/CO ratio	0.67/1
Space velocity	2.0 NL/g cat/h
Temperature	270 °C
Pressure	1.48 MPa

Variation of synthesis gas conversion with time on stream after different pretreatments



HU CSTR Set Up

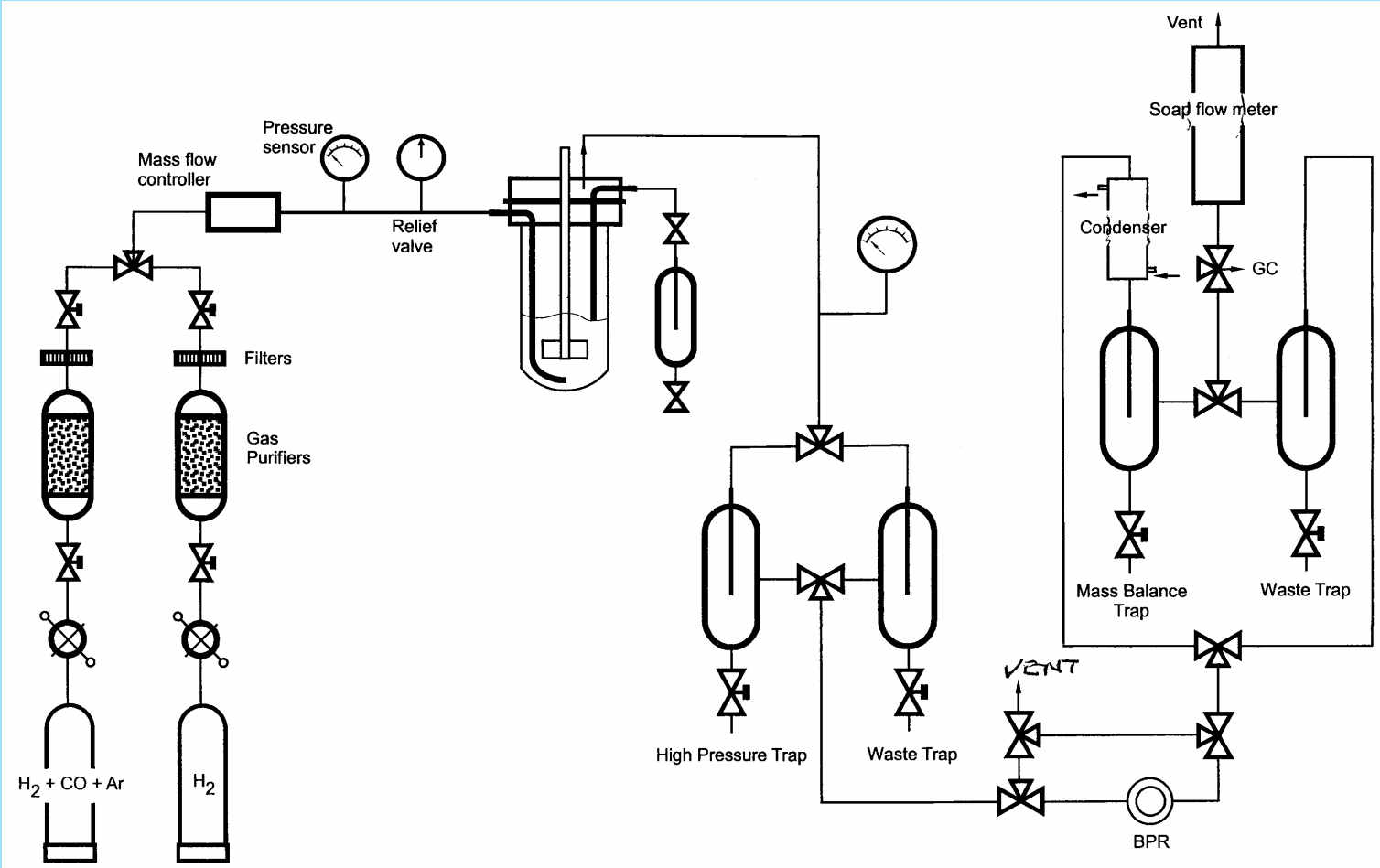
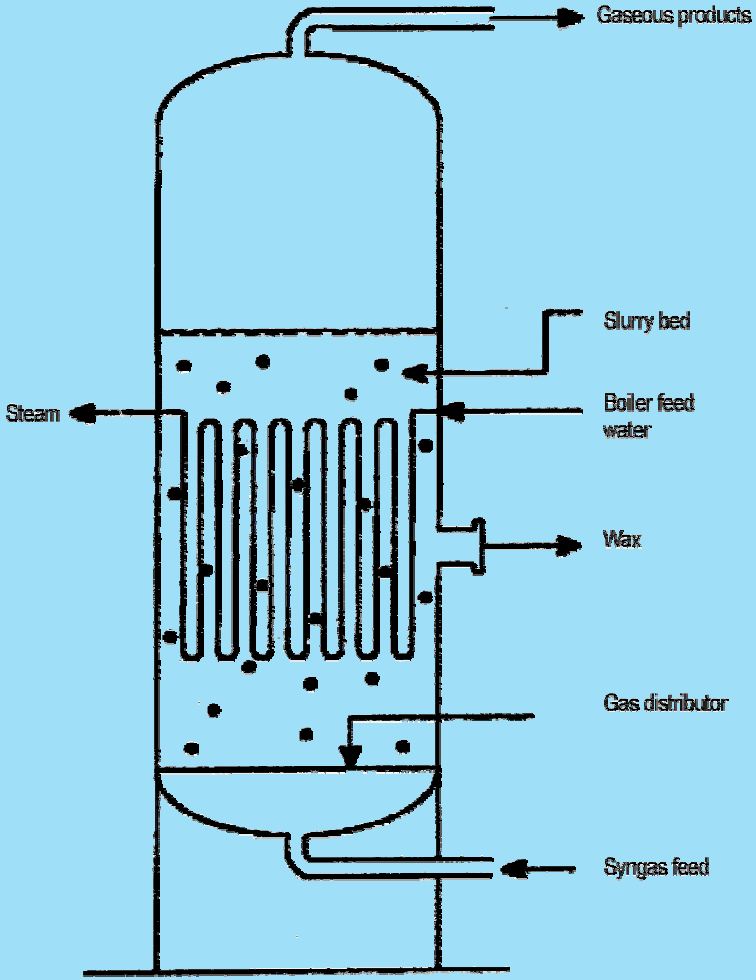


Figure 5. Schematic of Slurry F-T Reactor

Slurry Bubble Column Reactor

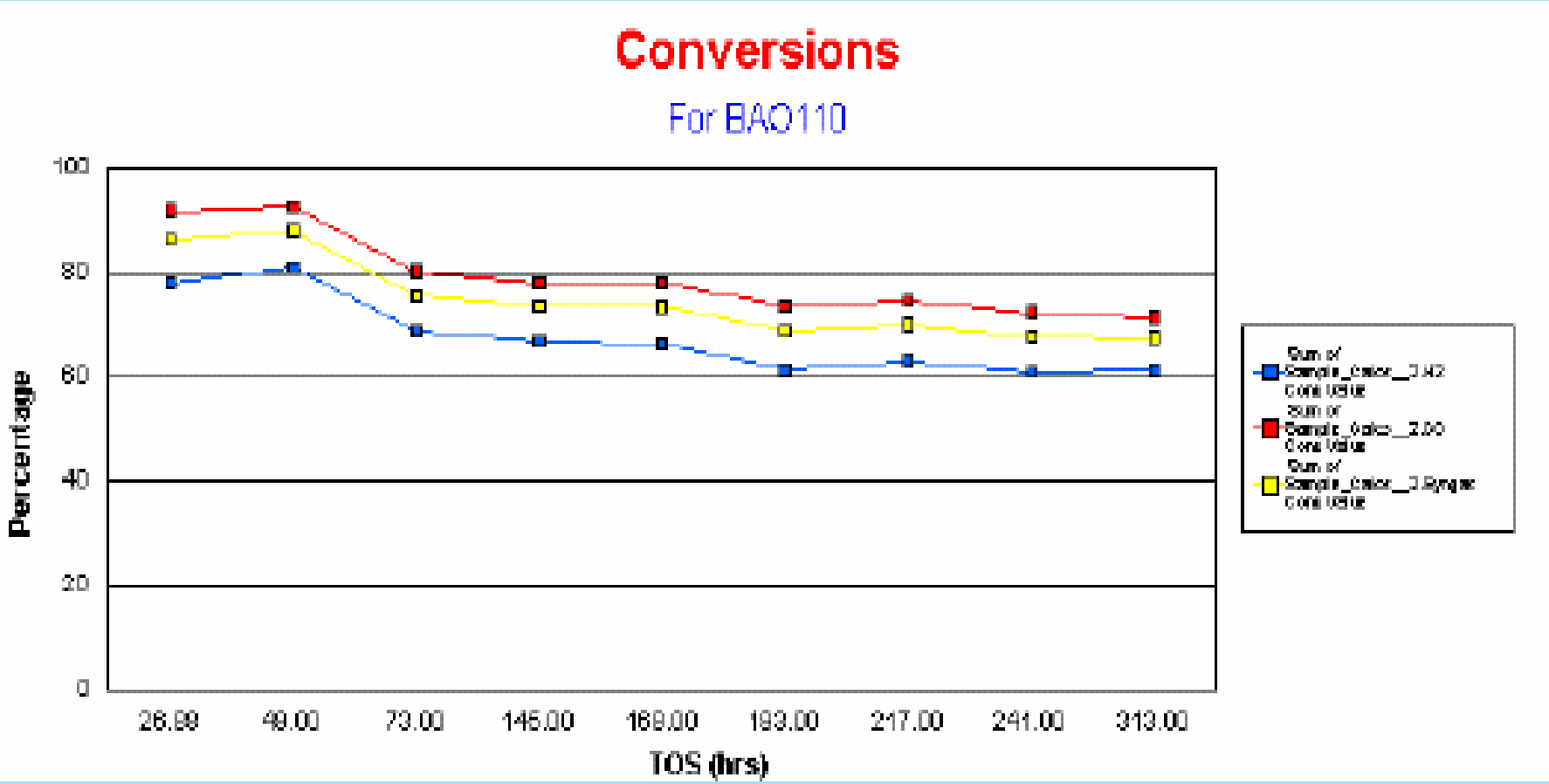


CSTR Experimental Condition

- The conditions for testing are as follows:

CSTR Stirrer Speed (rev/min)	500
Temperature (^oC)	260^oC
Pressure (Mpa)	2.0
Space velocity (NL/gcat/h)	2.0
Syngas Composition	H_2/CO-0.67
Activation	0.1 Mpa, H_2/CO = 0.67, 280^oC for 12 h

CSTR Results



Summary

- Active iron catalysts prepared in 50+ gram quantities by spray drying
- CO conversion >95% achieved
- Silica content around 12 wt% showed the lowest attrition resistance
- The activity of the syngas (H_2/CO = 0.67) pretreated catalysts was the highest among all the pretreatment procedure used

Future Work

- Continue to improve catalyst performance
- Testing of the best catalysts in a CSTR

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- Texas A&M University – Dr. Dragomir B. Bukur
- University of Kentucky – Dr. Burton Davies
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